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PREPARATION AND CHARACTERIZATION OF $Cd_{1-x}Fe_xSe$ SINGLE CRYSTALS

by

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PREPARATION AND CHARACTERIZATION OF $Cd_{1-x}Fe_xSe$ SINGLE CRYSTALS

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ABSTRACT

The limit of substitution of iron for cadmium in CdSe was determined by x-ray diffraction of polycrystalline samples to be 11.5 ± 1 mole percent. Single crystals of $Cd_{1-x}Fe_xSe$ were grown by CVT and by a modified Bridgman method. The magnetic susceptibility of crystals grown by both methods displayed field-independent behavior. Measurements of susceptibility as a function of temperature showed Curie-Weiss behavior with net antiferromagnetic interactions. Bridgman-grown crystals have room temperature resistivities at least 10^3 ohm-cm higher than that of the CVT grown crystals (1700 ohm-cm). The iron concentration of Bridgman-grown crystals was homogeneous in a radial direction, but showed 0.5 - 0.8 mole percent change in iron concentration along the length of the boule.

MATERIALS INDEX: Cadmium iron selenide; Single crystal growth;
Magnetic properties

Introduction

The site preference of Fe(II) d^6 in oxide systems is predominantly that of octahedral coordination. However, in certain chalcogenides, Fe(II) can be stabilized on a tetrahedral site. Early optical studies indicated that Fe(II) could be substituted for Zn(II) in sphalerite (1), and for Cd(II) in CdS (2). Recently the photoluminescence (3), magnetic susceptibility (4), and specific heat (4) of $Cd_{1-x}Fe_xSe$ were studied. These reports indicated that Fe(II) could be stabilized on tetrahedral sites in the wurtzite structure of CdSe.

This study determines the limit of substitution of iron for cadmium in polycrystalline CdSe as well as comparing the electrical and magnetic properties of single crystals of the phase $Cd_{1-x}Fe_xSe$ grown by chemical vapor transport and by a modified Bridgman method.

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Experimental

Polycrystalline samples were prepared by using stoichiometric amounts of cadmium, (Cominco EM 8001, 99.999%), selenium (UMC 23333 99.999%), iron (Leico 46987) pre-reduced in Ar/H_2 (85/15) and 1 mg iodine (sublimed, Deepwater Chemical Co. Ltd. ACS reagent 99.9%) per gram of charge. The samples were sealed in evacuated 12 mm silica tubes and heated in the following manner: 400°C 6 hrs, 500°C 6 hrs, 600°C 96 hrs and 725°C for 24 hrs. The samples were ground in an agate mortar under a N_2 atmosphere prior to the 600°C heating, after 48 hrs at 600°C and before the 725°C heating. The samples were cooled with the furnace to room temperature before removal.

Crystal Growth

Chemical Vapor Transport. Polycrystalline $Cd_{.95}Fe_{.05}Se$ was placed in a silica tube (14 mm O.D. x 12 mm I.D.) which had been previously reworked to remove any irregularities which might become nucleation sites. The tube was evacuated to 2 microns of Hg for a period of 6 hrs. Freshly sublimed iodine was introduced as the transport agent at a concentration of 8 mg/ml of tube volume. After sealing, the tube was placed in a three-zone furnace. The charge was pre-reacted at 570°C for 15 hrs with the growth zone maintained at 800°C in order to prevent transport. The furnace was then equilibrated to give an isothermal zone across the reaction tube and was then programmed to give a temperature gradient of 750-725°C. Crystals were allowed to grow at the cooler zone for 6 days. The tubes were allowed to cool with the furnace. The crystals were then removed and washed in acetone.

Bridgman Growth. Boules of $Cd_{1-x}Fe_xSe$ weighing approximately 7 grams were grown using a modified Bridgman technique. The starting material was a polycrystalline charge of $Cd_{.95}Fe_{.05}Se$, an additional 5 mole percent of selenium and one mg of iodine were added per gram of total charge. The apparatus used for the evacuation and sealing of the reagents was similar to that used by Ridgley et al. (5).

After the growth ampoule was sealed, it was joined to a silica tube and suspended in a vertical furnace. The connected silica tube was attached to a 4 rpm motor which rotated the sample throughout the entire growth process to ensure uniform heating of the sample. The ampoule was brought to 1225°C over a 24 hr period and allowed to equilibrate at 1225°C for 8 hrs to homogenize the melt. Subsequent growth was carried out by lowering the ampoule 2.54 cm/24 hrs through a gradient of 100°C in 96 hrs. The furnace was then turned off and allowed to cool to room temperature before removal of the ampoule.

Each boule was annealed in the same ampoule as the growth occurred. The ampoule was placed in an isothermal zone of a furnace at 825°C for 12 days and then slow-cooled to 600°C before turning off the furnace. The ampoule was allowed to cool with the furnace to room temperature before removal. The boule was then sliced into 1 mm wafers using a South Bay Technology, Inc. Model 650 low speed diamond wheel saw. The topmost 5 mm of the boule contained the excess selenium and was therefore discarded.

X-Ray Analysis

Finely ground samples were analyzed on a Philips diffractometer using monochromated high intensity $CuK\alpha_1$ (λ = 1.5405Å) radiation. The diffraction patterns were taken in the range of $12° < 2\theta < 72°$ with a scan rate of $1°$ 2θ/min and a chart speed of 30 in/hr. Precision slow scans (scan rates of $0.25°$ 2θ/min) were used to obtain data necessary for the determination of the cell constants.

Magnetic Measurements

Magnetic susceptibilities were measured using a Faraday balance (6) at a field strength of 10.4 kOe. The susceptibility was measured from 77 to 295 K. Honda-Owens (field dependency) measurements were carried out at 77 and 295 K. The data were then corrected for the core diamagnetism of CdSe.

Electrical Measurements

The electrical measurements were made using the van der Pauw technique (7). Flat and parallel surfaces were established with 600 grit abrasive paper under distilled water. Electrical contacts were made by the ultrasonic soldering of indium directly onto the edge of the samples, and their ohmic behavior was established by measuring their current-voltage characteristics.

Results and Discussion

Polycrystalline samples of $Cd_{1-x}Fe_xSe$ were prepared directly from the elements. X-ray diffraction patterns indicated that the products were of single phase and could be indexed on the basis of a hexagonal unit cell (8). These samples exhibited field dependent behavior; however, the spontaneous moment could be quenched by the addition of a small quantity of I_2.

Standard samples of $Cd_{1-x}Fe_xSe$ containing 0, 2, 5, 7.5, 10, 13, and 15 mole percent iron were prepared from the elements and with the addition of 1 mg I_2/g charge. These standard samples were x-rayed to obtain cell parameters which were used to calculate cell volumes. The cell volume was plotted as a function of iron concentration as shown in Fig. 1. At concentrations of less than 11.5 mole percent, the cell volume decreased linearly with increasing amounts of iron. This indicated that the smaller Fe^{+2} was substituted for the larger Cd^{+2} as desired. The cell volumes of the 13 and 15 percent sample did not change within experimental error ($\pm$ 0.005 Å in the a parameter, and $\pm$ 0.01 Å in the c parameter). The data shown in Fig. 1 indicate that the solubility limit of iron in polycrystalline CdSe is 11.5 $\pm$ 1 mole percent.

The room temperature susceptibilities of the 2, 5, 7.5 and 10 mole percent iron samples were plotted as a function of iron concentration as shown in Fig. 2. Using this plot, the iron concentration of a single crystal could be determined from the room temperature susceptibility.
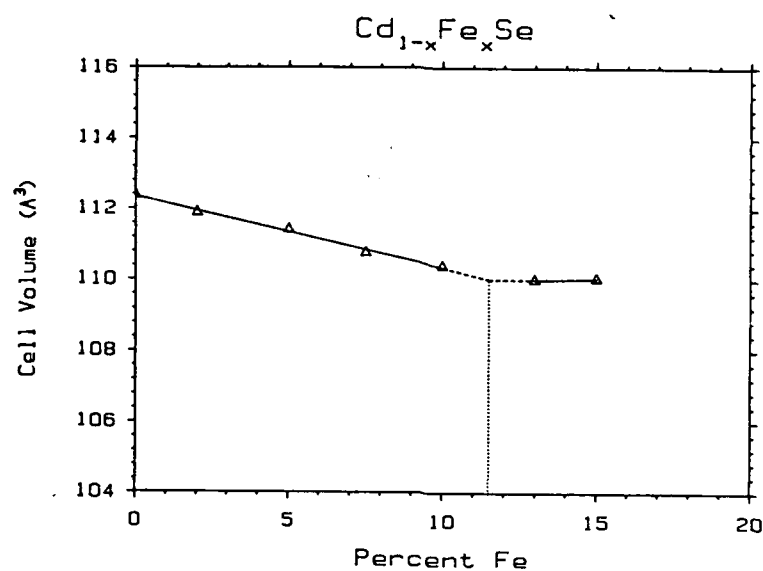
Fig. 1. Variation of cell volume with nominal iron concentration in polycrystalline $Cd_{1-x}Fe_xSe$.
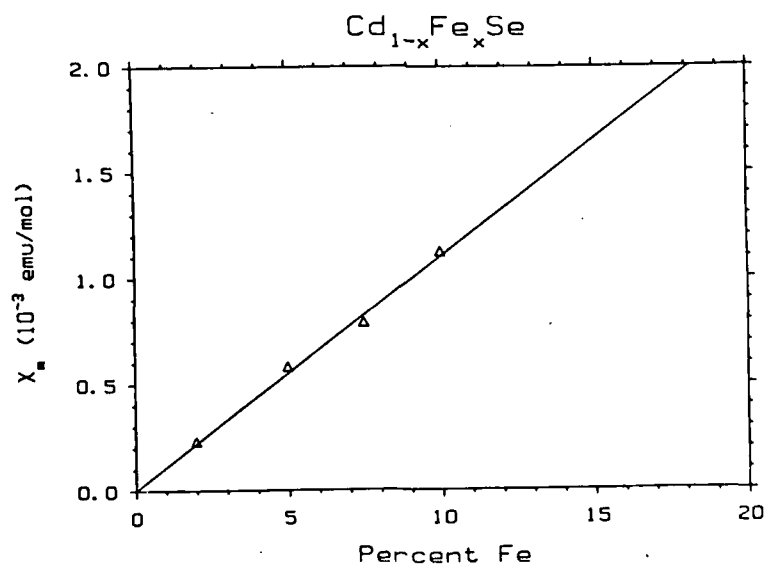

Fig. 2. The linear relationship between magnetic susceptibility and iron concentration as derived from measurements on polycrystalline $Cd_{1-x}Fe_xSe$ standard samples at ambient temperature.

$$Cd_{.98}Fe_{.02}Se$$
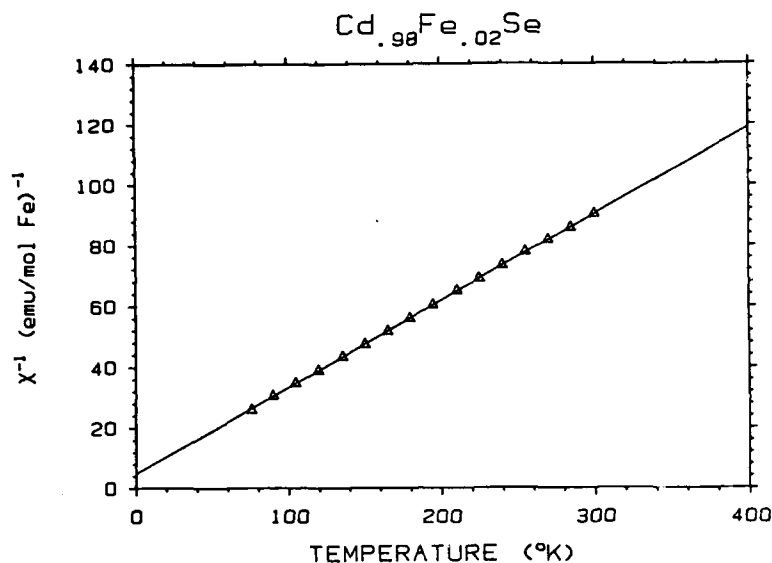

Fig. 3. Inverse magnetic susceptibility of polycrystalline $Cd_{.98}Fe_{.02}Se$ as a function of temperature.

The magnetic susceptibility of $Cd_{.98}Fe_{.02}Se$, plotted as a function of temperature, showed paramagnetic behavior with net antiferromagnetic interactions (Fig. 3). The moment of this sample was determined to be 5.3 BM with a Weiss constant of -17.1 K. At higher concentrations of iron, the moment increases and the net antiferromagnetic interactions appear to increase. For a polycrystalline sample of $Cd_{.95}Fe_{.05}Se$, the moment was 5.6 BM with a Weiss constant of -41.2 K. The experimentally determined moment is higher than the spin-only value of high spin Fe^{+2} in tetrahedral sites (4.9 BM). However, both the moment and the Weiss constant for the 5 mole percent sample are in good agreement with experimental values reported by Lewicki et al. for single crystals of the same composition (4).

Single crystals of $Cd_{1-x}Fe_xSe$ were grown by chemical vapor transport and by a modified Bridgman method. A crystal grown by each method was chosen to compare their magnetic and electrical properties. The sample grown by Bridgman was a wafer cut from the bottom one-third of a boule and had a composition of $Cd_{.957}Fe_{.043}Se$. It should be noted that the iron concentration of the Bridgman-grown crystals was homogeneous in a radial direction, but the upper two-thirds contained less iron, with the upper sections having a composition of $Cd_{.962}Fe_{.038}Se$. The CVT crystal had a composition of $Cd_{.955}Fe_{.045}Se$. Both crystals appeared black and could be indexed on the basis of a hexagonal cell. The magnetic susceptibility of both crystals displayed field independent behavior and, when plotted as a function of temperature, the susceptibility showed Curie-Weiss behavior with net antiferromagnetic interactions.

The room temperature resistivity of the CVT crystal was determined to be 1700 ohm-cm. The Bridgman sample had a room temperature resistivity of greater than 10^6 ohm-cm. The decreased resistivity of the CVT crystal may be due to the incorporation of some of the iodine present during the growth process.

Conclusions

Fe(II) can be substituted for Cd up to 11.5 mole percent in the tetrahedral CdSe structure. The magnetic susceptibility measurements confirm the existence of $3d^6$ Fe(II) in a single homogeneous phase which can be represented as $Cd_{1-x}Fe_xSe$. Single crystal growth could be achieved both by Bridgman and by chemical vapor transport using iodine as the transport agent.

Acknowledgments

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